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14. ABSTRACT

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Report Title

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Enter List of papers submitted or published that acknowledge ARO support from the start of the project to the date of this printing. List the papers, including journal references, in the following categories:

(a) Papers published in peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in peer-reviewed journals:

(b) Papers published in non-peer-reviewed journals (N/A for none)

Received Paper

TOTAL:

Number of Papers published in non peer-reviewed journals:

(c) Presentations

Number of Presentations: 0.00

Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Non Peer-Reviewed Conference Proceeding publications (other than abstracts):

Peer-Reviewed Conference Proceeding publications (other than abstracts):

Received Paper

TOTAL:

Number of Peer-Reviewed Conference Proceeding publications (other than abstracts):

(d) Manuscripts

Received Paper

TOTAL:

Number of Manuscripts:

Books

Received Book

TOTAL:

Received Book Chapter

TOTAL:

Patents Submitted

Patents Awarded

Awards

Graduate Students

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Post Doctorates

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Faculty Supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Names of Under Graduate students supported

NAME	PERCENT_SUPPORTED

FTE Equivalent:
Total Number:

Student Metrics

This section only applies to graduating undergraduates supported by this agreement in this reporting period

The number of undergraduates funded by this agreement who graduated during this period: 0.00

The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and will continue to pursue a graduate or Ph.D. degree in science, mathematics, engineering, or technology fields:...... 0.00

Number of graduating undergraduates who achieved a 3.5 GPA to 4.0 (4.0 max scale):...... 0.00

Number of graduating undergraduates funded by a DoD funded Center of Excellence grant for Education, Research and Engineering:...... 0.00

The number of undergraduates funded by your agreement who graduated during this period and intend to work for the Department of Defense 0.00

The number of undergraduates funded by your agreement who graduated during this period and will receive scholarships or fellowships for further studies in science, mathematics, engineering or technology fields:...... 0.00

Names of Personnel receiving masters degrees

NAME

Total Number:

Names of personnel receiving PHDs

NAME

Total Number:

Names of other research staff

NAME	PERCENT_SUPPORTED

FTE Equivalent:

Total Number:

Sub Contractors (DD882)

Inventions (DD882)

Scientific Progress

PI Maria and his graduate team constructed a dua-chamber PVD system that can deposit a varity of inorganic thin films by sputtering, e-beam evaporation, and laser ablation. The PI leveraged existing resources (i.e., spare parts, existing lasers, in-house design, etc...) under this DURIP to create a system that is substantially more capable than otherwise possible with this DURIP support. The instrument is currently operational, has been making thin film laminates, and works as proposed by the PI in the original proposal. A schematic of the instrument and a photograph is included in the attachments section.

The PI notes that while this is a final report, there was a request for NCE submitted by NCSU in June 2015 as system construction is not 100% complete. It was necessary to reserve some funding until the films produced by the system were characterized so that any modification to improve them could be made. It appears that NCSU was errant in the submission.

Technology Transfer

none to report

DESCRIPTION OF INSTRUMENTATION

A versatile physical vapor deposition system (PVD) that accommodates sputtering, e-beam evaporation, thermal evaporation, pulsed laser deposition, and ion-assisted deposition was constructed during this DURIP program. The configuration is optimized for nanolaminate deposition, but it includes design elements to provide compatibility with additional DoD programs in the Maria Labs for maximum impact on existing and future research programs. Fig. 1 illustrates a schematic of the instrument proposed. The features of importance, and their specific role in material synthesis are bulletized below. It is important to note that maximum added value was achieved in this program by incorporating new DURIP components with existing infrastructure in the Maria labs. This combination of new and existing equipment optimized overall capabilities available from DURIP funding.

1. **LOAD-LOCK:** Minimizing contamination, controlling interfaces, and maximizing reproducibility are particularly important for nanolaminates research. Each of these objectives is enhanced by a load locked system where the sources and deposition chamber are not exposed to atmospheric conditions (with the exception of system maintenance). As such, the proposed system includes a manual load-lock capable of transferring a 4" diameter wafer. Load locking a system also dramatically reduces pump-down times, and in turn, the potential throughput of such a multi-purpose deposition tool.

2. **e-BEAM EVAPORATION SOURCE:** The e-beam evaporation source is by far the most expensive component of this PVD tool. E-beam sources, however, are particularly versatile because they can create physical vapors of extremely refractory metals and oxides at very low pressures without energetic bombardment. Moreover, they provide excellent deposition uniformity and can use very inexpensive source materials. In contrast, sputtering can produce thin films of the most refractory metals, like W, however one must use mTorr background pressures of Ar gas (which can introduce contaminants and can be incorporated into the growing layers). Furthermore, sputtering requires a precision-machined target, which can present a substantial expense, particularly when target diameters exceed 2". Adding an e-beam source to the Maria Group laboratory expands the repertoire of available materials and, in a number of cases, the ability to better tailor structure and properties. The e-beam source contains 6 copper wells that can be rotated to a position under the electron beam. As such, one set of electron optics can produce 6 different compositions without breaking vacuum to exchange the source material. Currently, the e-beam is loaded with Zr, Al, Ti, Ni, Pt, and Mg. These are primary components of the reactive nanolaminates for which this system is intended primarily.

3. **MAGNETRON SOURCE:** Two magnetron sources complement the e-beam for co-deposition of alloys and for preparing metal oxides. E-beam evaporators can be used for reactive deposition of metal oxides from a metal flux and an oxygen background gas, however those oxygen source materials like CuO (by nature of their comparatively weak bonding) require high oxygen pressures to achieve the desired oxidation state. High oxygen pressures are not compatible with e-beam evaporation due to filament oxidation and limitations imposed by scattering between the metal flux and the ambient gas prior to metal atoms arriving on the substrate. Magnetron sources also provide a tunable component of energetic bombardment, which under the correct circumstances enable one to tune film microstructure.

4. **PLD:** The configuration we produced includes a sister chamber to accommodate pulsed laser deposition target rotator. PLD is unique with respect to other PVD methods in its access to high background pressures. This allows one to achieve very high partial pressures of active O and N species, and thus high values of supersaturation. This in turn allows one to control anion stoichiometry to an extent that challenges most other methods, and this is particularly important for the PI's nanolaminates program which relies on preparing oxides with will controlled oxygen stoichiometry. The high-pressure environment possible in PLD also allows one to have many gas-phase collisions that thermalize kinetic energy of the depositing species. Such "soft landing" environments are important when attempting to control reactive interfaces. PLD can achieve such conditions with very refractory materials that cannot be evaporated, while eliminating the energetic bombardment associated commonly with sputtering. The PLD rotator is compatible with the existing excimer laser used by the Maria Group.

5. **PLASMA SOURCE PORTS:** The chamber includes ports to accept future plasma sources. Plasma sources are convenient means of metal oxide layers from materials with relatively high vapor pressures. The presence of active oxygen enhances the ability to fully oxidize high vapor pressure cations, which otherwise have a tendency to re-evaporate. Practically, this extends the range of possible materials, which can be made, and improves ones ability to achieve the desired oxygen stoichiometry values.

6. **A COMMON LOAD LOCK:** I the near future, the two sister chambers will be served by a common load lock. This will enable sample hand-offs between the two systems, and further the ability to integrate between dissimilar materials and to optimize interface quality since a wide variety of interfaces can be made without exposing samples to atmosphere between the layers.

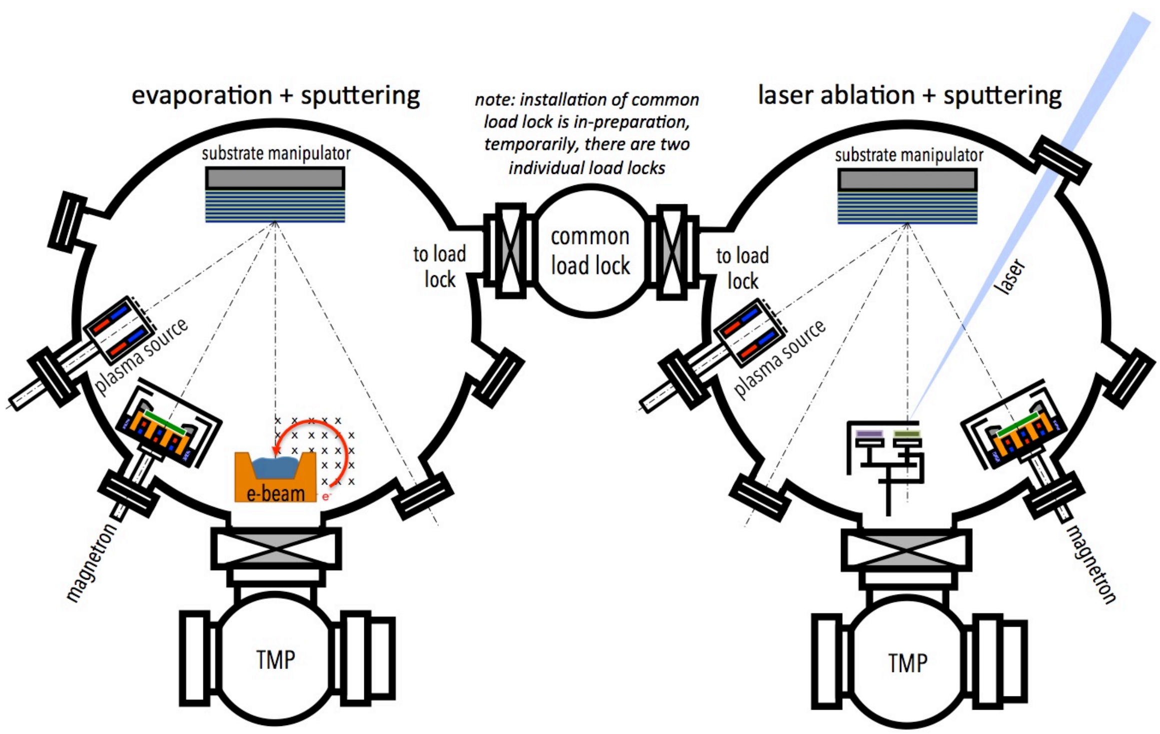

Figure 1: Schematic illustration of the two-chamber PVD system at NCSU

Figure 2: Photograph of the two-chamber PVD system at NCSU

PRIMARY INTENDED USAGE OF INSTRUMENTATION

PI Maria is leading a collaborative ARO-funded experimental-computational investigation of reactive nanocomposite structures identified as attractive new energetic materials with the potential for tunable power via engineered ignition. The material combinations belong to a family of metal/metal oxide nanolaminates that are thermodynamically predisposed to the rapid release of chemical energy via ion exchange. The energy densities are up to four times larger than values accessible to conventional organics (*i.e.*, RDX) and there are electrical ignition possibilities that span local to volumetric geometries. Consequently one can predict sensibly a new generation of energetic composites that, in conjunction with conventional materials, create a new capability to design and fabricate munitions with tunable lethality and potentially lower mass.

The nanocomposites comprise oxygen sources like CuO and oxygen sinks like Cr. Material combinations that support this exchange are historically categorized as a thermites, and though known for many years and optimized for temperature generation, opportunities for high power remain underexplored.

The new PVD system supported by this DURIP program is designed to research nanothermite laminate structures with a higher level of uniformity and control than was possible previously at NCSU. This will replace an existing system that was utilized previously for similar tasks. The

primary advantages of this new system and their impact on Maria Group programs are summarized as follows:

- Higher purity materials are now possible with e-beam deposition, especially for the reactive metals;
- The system features improved quantitative thickness control due to an included crystal monitor;
- Substantially larger samples can be produced due to a larger chamber and a longer source to substrate distance. This will enhance throughput and provide more opportunities to provide samples to collaborating groups that also have related ARO programs focusing on energetic materials;
- Larger pumps and cleaner vacuum systems expedite sample synthesis;
- There are multiple sources in each chamber, this increases the sophistication of the laminates that can be made, i.e., we can now make three- and four-component multilayer stacks
- The new system features a high temperature substrate holder, this provides an additional level of control for film structure that was not available previously.

PI Maria will capitalize on these new capabilities and continue to explore energetic nanolaminates based on ion exchange with a focus on engineering rates of energy release by combining a detailed understanding of the defect equilibrium chemistry that controls transport with macroscopic design principles that control Joule heating and thermal energy partitioning.

IMPACT ON EDUCATION AND TRAINING

The PVD instrument proposed will impact education and training in three primary ways:

The Maria Group graduate and undergraduate students will be "executive" users, or those who's conduct research programs that depend primarily on materials prepared in the new instrument, and who are responsible for developing recipes, calibration metrics, and general maintenance. From the Maria Group, between 3 and 6 executive users are expected on average.

There will be a similarly sized cohort of graduate and undergraduate students form other groups on campus that will be secondary users. Students from Chemistry, Mechanical Engineering, Chemical Engineering, Textile Engineering, and Materials are among this group.

Throughout the academic year and summer term, multiple outreach activities aim to educate pre-college/graduate students about opportunities for careers in Materials Science and Engineering and other STEM disciplines. The Maria Group is a perennial participant in several, including the annual Materials Camp (a two week laboratory immersion program offered by the MSE department each summer for high school students) where utilize our showcase instruments to ensure the most substantive impact. The instrument we propose here will be integrated into each of these activities.

ESTIMATED USEFUL LIFE OF THE EQUIPMENT

Vacuum instrumentation is constructed from a combination of: 1) highly standardized structural components (*i.e.*, flanges, valves, adapters, *etc*…) that are in most cases seamlessly exchanged between systems, these components have essentially infinite lifetimes; 2) active electronic components like pressure gages, flow controllers, and temperature controllers that are also exchangeable, but have typical lifetimes on the order of 10 years (typically electronic parts fail and cannot be replaced after such times); and 3) active mechanical components like bellows, rotation feed-throughs, and low and high vacuum pumps which, if serviced regularly, have lifetimes of >20 years.

As such, the lifetime of the proposed instrument in its as-purchased form is at minimum 20 years. However, the value of the individual components is substantially longer. For high vacuum instruments, the most common lifetime is determined by the extent to which the intended purpose of the instrument can serve contemporary research needs. Once this time has elapsed, the interchangeability of the individual components allows them to be repurposed to address issues of modern interest. For example, the Maria Group is operating a nearly 30-year-old molecular beam epitaxy system, which was originally designed for GaAs, but converted in 2005 for oxide thin film growth.